

METHOD AND APPARATUS FOR TREATING A WASTE GAS  
CONTAINING FLUORINE-CONTAINING COMPOUNDS

BACKGROUND OF THE INVENTION

5 This invention relates to the treatment of a waste  
gas containing fluorine-containing compounds. More  
particularly, it relates to a method and an apparatus for  
efficient treatment of emissions from semiconductor  
fabrication plants, particularly from the steps of dry  
cleaning the inner surface of a fabrication apparatus  
10 and etching various kinds of deposited films with  
perfluorocarbons (PFCs) and halogenated hydrocarbons such  
as  $C_2F_6$ ,  $C_3F_8$ ,  $CHF_3$ ,  $SF_6$  and  $NF_3$ , said waste gases containing  
not only PFCs but also oxidizing gases such as  $F_2$ ,  $Cl_2$  and  
 $Br_2$ , acidic gases such as  $HF$ ,  $HCl$ ,  $HBr$ ,  $SiF_4$ ,  $SiCl_4$ ,  $SiBr_4$ ,  
15 and  $COF_2$ , as well as  $CO$ .

Semiconductor fabrication plants use many kinds of  
harmful gases that can potentially pollute the environment.  
PFCs contained in waste gases that typically result from  
the etching and CVD steps are suspected of causing global  
20 warning and it is urgently needed to establish an effective  
system for their removal.

Various breaking and recovery techniques have  
heretofore been proposed for PFC removal. Catalytic  
thermal decomposition is one of the breaking techniques and  
25 uses versatile compounds such as Pt catalyst, zeolite-base  
catalysts, activated charcoal, activated alumina, alkali  
metals, alkaline earth metals and metal oxides. However,  
none of these catalytic compounds have proved completely  
satisfactory.

30 The waste gases discharged from the semiconductor  
fabrication process contain not only PFCs but also  
oxidizing gases such as  $F_2$ ,  $Cl_2$  and  $Br_2$ , acidic gases such  
as  $HF$ ,  $HCl$ ,  $HBr$ ,  $SiF_4$ ,  $SiCl_4$ ,  $SiBr_4$  and  $COF_2$ , as well as  $CO$ ;  
however, no method has yet been established that can  
35 realize a thorough and effective treatment of these harmful  
gases.

If one wants to treat oxidizing gases such as  $F_2$ ,  $Cl_2$   
and  $Br_2$  by a wet method, thorough treatment cannot be

achieved by the sole use of water. If alkali agents or reducing agents are also used, not only process control but also the treatment apparatus becomes complicated and, in addition, the cost of treatment increases.

5 To remove CO, it has to be decomposed with oxidizers such as those based on Cu or Mn. As for PFCs, it has been proposed to use alumina as an agent for removing them (Japanese Patent Public Disclosure No. 286434/1998) and this method is characterized by contacting C<sub>2</sub>F<sub>6</sub> with  
10 molecular oxygen. However, the lifetime of alumina is very short and the throughput or the amount of C<sub>2</sub>F<sub>6</sub> that can be treated for 100% decomposition is only 4.8 L/L; what is more, no effective way has been proposed to deal with CO that occurs as a by-product of C<sub>2</sub>F<sub>6</sub> decomposition, still  
15 less for the oxidizing gases and acidic gases that occur concomitantly with PFCs.

#### SUMMARY OF THE INVENTION

The present invention has been accomplished under these circumstances and has as an object providing a method  
20 for treating waste gases containing fluorine-containing compounds which achieves high percent decomposition of PFCs, which proves effective for a prolonged time and which simultaneously realizes effective removal of oxidizing gases, acidic gases and CO that are contained in the waste  
25 gases.

Another object of the invention is to provide an apparatus for implementing this method.

The first object of the invention can be attained by a method for treatment of a waste gas containing fluorine-  
30 containing compounds which comprises the steps of separating the solids from the waste gas, adding H<sub>2</sub> and/or H<sub>2</sub>O or H<sub>2</sub> and/or H<sub>2</sub>O and O<sub>2</sub> as a decomposition assist gas, thermally decomposing the waste gas by contact with  $\gamma$ -alumina at usually at 500 - 1000°C, preferably 600 - 900°C, more  
35 preferably 700 - 900°C, and removing acidic gases from the decomposed waste gas.

In this method, the waste gas containing fluorine-containing compounds may be a waste gas from a semiconductor

fabrication process that contains not only perfluorocarbons and fluorinated hydrocarbons but also oxidizing gases, acidic gases and CO.

The second object of the invention can be attained  
5 by an apparatus for treatment of a waste gas containing  
fluorine-containing compounds which comprises a solids  
treating means for separating the solids from a waste gas  
containing fluorine-containing compounds, an addition means  
for adding H<sub>2</sub> and/or H<sub>2</sub>O or H<sub>2</sub> and/or H<sub>2</sub>O and O<sub>2</sub> as a  
10 decomposition assist gas to the waste gas leaving the solids  
treating means, a thermal decomposing means that is packed  
with γ-alumina heated at 600 - 900°C and which thermally  
decomposes the waste gas to which the decomposition assist  
gas has been added, an acidic gas treating means for  
15 removing acidic gases from the thermally decomposed waste  
gas, and channels for connecting these means in sequence.

In this treatment apparatus, a water scrubber may be  
used as the solids treating means or the acidic gas  
treating means. This treatment apparatus may have not only  
20 an air ejector capable of adjusting the pressure in the  
apparatus through which the waste gas passes but also an  
FT-IR analyzer for controlling the emission density of the  
treated gas.

The first step in the method of the invention for  
25 treating a waste gas containing fluorine-containing  
compounds is passing the waste gas through a solids  
treating means such as a water scrubber. The exit gas is  
passed through a thermal decomposing means packed with  
γ-alumina heated at 500 - 1000°C, preferably 600 - 900°C, and  
30 more preferably 700 - 900°C, with H<sub>2</sub> and/or H<sub>2</sub>O or H<sub>2</sub> and/or  
H<sub>2</sub>O and O<sub>2</sub> being added as a decomposition assist gas, so  
that PFCs, oxidizing gases and CO are completely decomposed  
into acidic gases and CO<sub>2</sub>. The generated acidic gases are  
removed with an acidic gas treating means such as a water  
35 scrubber.

The invention may incorporate not only an air ejector  
capable of adjusting the pressure in the apparatus through  
which the waste gas passes but also an FT-IR analyzer for

controlling the emission density of the treated gas.

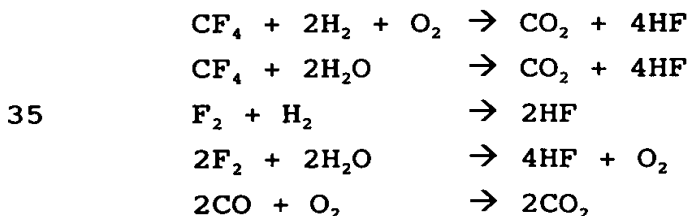
#### BRIEF DESCRIPTION OF THE DRAWING

Fig. 1 is a flowsheet for the waste gas treatment apparatus of the invention.

#### 5 DETAILED DESCRIPTION OF THE INVENTION

The present invention is described below in detail. In the first step, a waste gas containing PFCs, oxidizing gases, acidic gases and CO is passed through a solids treating means such as a water scrubber in order to remove  
10 not only the solids such as  $\text{SiO}_2$  in the waste gas but also Si compounds such as  $\text{SiF}_4$ ,  $\text{SiCl}_4$  and  $\text{SiBr}_4$  that may potentially solidify in the thermal decomposing means at the next stage. If the waste gas is directly introduced into the thermal decomposing means without being passed  
15 through the solids treating means, clogging or other blocking problems will occur, potentially preventing the waste gas from smoothly flowing through the packed  $\gamma$ -alumina layer. The performance of  $\gamma$ -alumina may also deteriorate. By passing the waste gas through the solids  
20 treating means, the solids and the acidic gases containing Si compounds are removed whereas part of oxidizing gases such as  $\text{F}_2$ ,  $\text{Cl}_2$  and  $\text{Br}_2$  as well as all volumes of PFCs and CO are discharged.

The waste gas emerging from the solids treating means  
25 is then introduced into the thermal decomposing means so that it is decomposed through contact with  $\gamma$ -alumina heated at  $500 - 1000^\circ\text{C}$ , preferably  $600 - 900^\circ\text{C}$ , more preferably  $700 - 900^\circ\text{C}$ . On this occasion,  $\text{H}_2$  and/or  $\text{H}_2\text{O}$ ; or  $\text{H}_2$  and/or  $\text{H}_2\text{O}$  and  $\text{O}_2$  are added to the waste gas as a decomposition assist  
30 gas so that the components of the waste gas are decomposed into acidic gases and  $\text{CO}_2$  according to the following reaction schemes:



Thus, PFC reacts with  $H_2$  and  $O_2$  or  $H_2O$  to be decomposed into  $CO_2$  and  $HF$ . Acidic gases such as  $F_2$  react with  $H_2$  or  $H_2O$  to be decomposed to another acidic gas  $HF$ . Carbon monoxide ( $CO$ ) is oxidized to  $CO_2$ .

5 As for PFC,  $H_2$  or  $H_2O$  is added in moles at least equal to the moles necessary for the F atoms in the PFC to be converted to  $HF$  and  $O_2$  is added in moles at least equal to the moles necessary for the C atoms in the PFC to be converted to  $CO_2$ . Preferably,  $O_2$  is added in moles which  
10 are at least equal to the sum of one mole and the above-defined minimum number of moles. As for oxidizing gases,  $H_2$  is introduced in moles at least equal to the moles necessary for the halogen atoms (X) in the oxidizing gas to be converted to an acidic gas (HX).

15 The waste gas leaving the thermal decomposing means only contains the acidic gases (HX) and  $CO_2$  and by subsequent treatment with an acidic gas treating means such as a water scrubber, the acidic gases are completely removed.

20 The alumina to be used in the invention may have a  $\gamma$ -crystalline structure without a uniform pore distribution. While the shape of the alumina is not limited in any particular way, spheres are easy to handle and, hence, preferred. To the extent that will not unduly increase the  
25 resistance to the passage of the waste gas, the particle size of  $\gamma$ -alumina should be as small as possible, preferably between 0.8 mm and 2.6 mm. The  $\gamma$ -alumina may be held at between  $500^\circ C$  and  $1000^\circ C$ , preferably  $600^\circ C$  and  $900^\circ C$  and more preferably  $700^\circ C$  and  $900^\circ C$  during the passage of the waste  
30 gas.

The solids treating means and the acidic gas treating means are preferably a packed column or a spray column on the condition that they are adapted to spray water. The thermal decomposing means should be adapted to permit the  
35 introduction of  $H_2$  and/or  $H_2O$  or  $H_2$  and/or  $H_2O$  and  $O_2$  as a decomposition assist gas.

Fig. 1 is a flowsheet for the waste gas treatment apparatus of the invention. It generally comprises the

solids treating means 1, the  $\gamma$ -alumina packed layer 2, the thermal decomposing means 3, a cleaning water circulating pump 4, the acidic gas treating means 5, an FT-IR analyzer 6, an air ejector 7 and a bypass valve 8.

5 A waste gas 9 containing PFCs, oxidizing gases, acidic gases and CO is first passed through the spray column (solids treating means) 1 so as to remove the solids and Si compounds. The waste gas is then passed through the thermal decomposing means 3 which is also supplied with  $H_2$ ,  
10  $O_2$  and  $H_2O$  to decompose the PFCs, oxidizing gases and CO into acidic gases and  $CO_2$ . The acidic gases are removed by passage through the next spray column (acidic gas treating means) 5, from which the treated gas 10 emerges.

The air ejector 7 is installed to control the pressure  
15 in each of the treating means and the FT-IR analyzer 6 is provided to monitor the treated gas.

Spray water 11 is introduced into the acidic gas treating means 5 and the spent water is forced to the solids treating means 1 with the cleaning water circulating  
20 pump 4; the water is used in spraying there and discharged as wastewater 12.

The following examples are provided for the purpose of further illustrating the present invention but are in no way to be taken as limiting.

25 Example 1

A quartz column of 25 mm $\phi$  was packed with  $\gamma$ -alumina to a height of 100 mm. The  $\gamma$ -alumina was a commercial product of Mizusawa Kagaku K.K. (NEOBEAD GB-08) having a particle size of 0.8 mm. The quartz column was installed in a  
30 ceramic electric furnace and the alumina layer was heated at 800°C.

In addition to  $CF_4$  diluted with  $N_2$  gas,  $H_2$  and  $O_2$  were supplied as decomposition assist gases, the amount of  $H_2$  being such that the number of H atoms was at least equal to  
35 the number of F atoms in  $CF_4$  and the amount of  $O_2$  being at least equimolar to the amount of  $H_2$  introduced. These gases were flowed into the column at a total rate of 408 sccm and their entrance concentrations were 1% ( $CF_4$ ), 3.0%

(H<sub>2</sub>) and 5.7% (O<sub>2</sub>).

In order to evaluate the performance of the treatment system, the exit gas was analyzed periodically and the passage of the CF<sub>4</sub> gas was stopped when the removal of CF<sub>4</sub> dropped below 98%. The throughput was determined from the amount of CF<sub>4</sub> that had been passed through the system. The analysis of CF<sub>4</sub> and other gases was conducted with a gas chromatographic apparatus equipped with a mass detector.

As it turned out, the removal of CF<sub>4</sub> dropped to 98% when its passage continued for 920 min. At this point in time, the throughput as determined from the quantity of the supplied CF<sub>4</sub> was 77 L/L. Throughout the experiment, the concentration of CO emission was below the tolerable level (25 ppm).

#### Comparative Example 1

An experiment was conducted using the same equipment as in Example 1 that was packed with the same  $\gamma$ -alumina in the same amount and heated to the same temperature. The total gas flow rate was 408 sccm; the feed gas was a mixture of N<sub>2</sub>-diluted CF<sub>4</sub> and SiF<sub>4</sub>; in addition, H<sub>2</sub> and O<sub>2</sub> were supplied as decomposition assist gases, the amount of H<sub>2</sub> being such that the number of H atoms was at least equal to the total number of F atoms in CF<sub>4</sub> and SiF<sub>4</sub> and the amount of O<sub>2</sub> being at least equimolar to the amount of H<sub>2</sub> introduced. These gases were flowed into the column at respective concentrations of 0.95% (CF<sub>4</sub>), 0.97% (SiF<sub>4</sub>), 5.3% (H<sub>2</sub>) and 6.0% (O<sub>2</sub>).

As it turned out, the removal of CF<sub>4</sub> dropped below 98% when the passage of the CF<sub>4</sub>/SiF<sub>4</sub> gas continued for 510 minutes. At this point in time, the throughput was 40 L/L, which was nearly one half the throughput for the case where only CF<sub>4</sub> gas was supplied. Throughout the experiment, the concentration of CO was below the tolerable level.

#### Example 2

An experiment was conducted using the same equipment as in Example 1 that was packed with the same  $\gamma$ -alumina in the same amount and heated to the same temperature. The total gas flow rate was 408 sccm; the feed gas was a

mixture of N<sub>2</sub>-diluted CF<sub>4</sub> and F<sub>2</sub>; in addition, H<sub>2</sub> and O<sub>2</sub> were supplied as decomposition assist gases, the amount of H<sub>2</sub> being such that the number of H atoms was at least equal to the total number of F atoms in CF<sub>4</sub> and F<sub>2</sub> and the amount of O<sub>2</sub> being at least equimolar to the amount of H<sub>2</sub> introduced. These gases were flowed into the column at respective concentrations of 0.92% (CF<sub>4</sub>), 1.1% (F<sub>2</sub>), 5.0% (H<sub>2</sub>) and 6.0% (O<sub>2</sub>).

As it turned out, the removal of CF<sub>4</sub> dropped below 98% when the passage of the CF<sub>4</sub>/F<sub>2</sub> gas continued for 25 hours. At this point in time, the throughput was 115 L/L, which was 1.51 times higher than the throughput for the case where only CF<sub>4</sub> gas was supplied. Throughout the experiment, the concentrations of CO and F<sub>2</sub> were below the tolerable levels (1 ppm for F<sub>2</sub>), provided that F<sub>2</sub> had been decomposed into HF.

#### Reference Example 1

An experiment was conducted using the same equipment as in Example 1 that was packed with the same  $\gamma$ -alumina in the same amount and heated to the same temperature. The total gas flow rate was 408 sccm; in addition to N<sub>2</sub>-diluted CO, O<sub>2</sub> was supplied in moles at least equal to the moles necessary for CO to be converted to CO<sub>2</sub>; their respective entrance concentrations were 1.4% (CO) and 5.7% (O<sub>2</sub>). Throughout the passage of the feed gas for 30 minutes, the concentration of CO was below the detection limit (2 ppm); all of CO had been oxidized to CO<sub>2</sub>.

#### Comparative Example 2

An experiment was conducted using the same equipment as in Example 1 that was packed with the same  $\gamma$ -alumina in the same amount and heated to the same temperature. The total gas flow rate was 408 sccm; in addition to N<sub>2</sub>-diluted CO, H<sub>2</sub>O was supplied at a rate of 0.090 mL/min which was 22 times as much as CO; the entrance concentration of CO was 1.3%.

As it turned out, 1000 ppm of CO leaked as a result of 15-min passage of the feed gas. Obviously, the concentration of CO could not be reduced to below the



tolerable level (25 ppm) by the sole addition of H<sub>2</sub>O.

Reference Example 2

An experiment was conducted using the same equipment as in Example 1 that was packed with the same  $\gamma$ -alumina in the same amount and heated to the same temperature. The total gas flow rate was 408 sccm; in addition to N<sub>2</sub>-diluted CO, H<sub>2</sub>O was supplied at a rate of 0.090 mL/min which was 18 times as much as CO and O<sub>2</sub> was supplied in moles at least equal to the moles necessary for CO to be converted to CO<sub>2</sub>; the entrance concentrations of CO and O<sub>2</sub> were 1.5% and 3.4%, respectively.

As it turned out, the concentration of CO had been reduced to below the detection limit (2 ppm) after the passage of the feed gas for 3 hours. Obviously, CO was oxidized to CO<sub>2</sub> by addition of O<sub>2</sub>.

Example 3

An experiment was conducted using the same equipment as in Example 1 that was packed with the same  $\gamma$ -alumina in the same amount and heated to 700°C. The total gas flow rate was 408 sccm; in addition to N<sub>2</sub>-diluted CF<sub>4</sub>, H<sub>2</sub>O was supplied at a rate of 0.040 mL/min which was 14 times as much as CF<sub>4</sub> and O<sub>2</sub> was supplied in moles at least equal to the moles necessary for the C atom in CF<sub>4</sub> to be converted to CO<sub>2</sub>; the entrance concentrations of CF<sub>4</sub> and O<sub>2</sub> were 0.89% and 3.0%, respectively.

As it turned out, the removal of CF<sub>4</sub> dropped below 98% when the passage of the feed gas continued for 23 hours. At this point in time, the throughput was 110 L/L, which was 1.4 times higher than the throughput of CF<sub>4</sub> treatment in the presence of added H<sub>2</sub> and O<sub>2</sub>. Throughout the experiment, the concentration of CO was below the tolerable level.

Comparative Example 3

In order to evaluate the effectiveness of the wet process in treating oxidizing gases and acidic gases, a water cleaning column (210 mm $\phi$  x 430 mm<sup>H</sup> with a Raschig ring packed to a height of 170 mm) was supplied with a waste gas at a total rate of 60 L/min and spray water at a

rate of 3.5 L/min. The waste gas was prepared from  $F_2$ ,  $SiF_4$  and  $Cl_2$  which had entrance concentrations of 1100 ppm, 1600 ppm and 5100 ppm, respectively. At the exit of the column,  $F_2$ ,  $SiF_4$  and  $Cl_2$  were detected at concentrations of 11 ppm, < 1 ppm, and 3300 ppm, respectively. Obviously,  $SiF_4$  was effectively treated but  $F_2$  and  $Cl_2$  leaked out.

#### Example 4

A water cleaning column (210 mm $\phi$  x 430 mm $^H$  with a Raschig ring packed to a height of 170 mm) was used as a solids treating means. This column was combined with a thermal decomposing means comprising a preheating chamber and a catalyst packed chamber and an acidic gas treating means which was the same as the water cleaning column. The exit gas leaving the acidic gas treating means was monitored with an FT-IR analyzer (Infinity 6000 of MATTSON) and the pressure in the experimental system was controlled with an air ejector of Daito Seisakusho K.K. The solids treating means and the acidic gas treating means were supplied with cleaning water at respective flow rates of 2 L/min and 4 L/min. The thermal decomposing means was supplied with air and pure water at respective flow rates of 10 L/min and 2.4 mL/min. The catalyst was 15 L of  $\gamma$ -alumina (NEOBEAD GB-08 of Mizusawa Kagaku K.K.)

A gas dryer (MD-70-72P of PERMAPUR) was installed ahead of the FT-IR analyzer for removing the moisture in the waste gas. Air was supplied into the air ejector at a rate of 30 L/min so that the pressure in the system was kept at a negative value of -0.5 kPa. A waste gas was introduced at a flow rate of 60 L/min and it was prepared from a  $N_2$  base containing  $CF_4$ ,  $SiF_4$ ,  $F_2$  and CO at respective concentrations of 0.5%, 0.3%, 0.3% and 0.3%. The waste gas was first passed through the solids treating means, then passed through the thermal decomposing means in the presence of added water and  $O_2$ , with the catalyst bed being heated at 700°C. The waste gas was subsequently passed through the acidic gas treating means and the treated gas was continuously analyzed by FT-IR. After the passage of the waste gas for 10 hours,  $CO_2$  was detected in an amount

### Example 5

15

20

According to the invention, harmful waste gases from the semiconductor fabrication process that contain PFCs, oxidizing gases, acidic gases and CO and which are a potential accelerator of global warming can be treated in such a way that high percent decomposition is maintained for a prolonged time.